THE FLUORINATION OF NON-POLAR HALIDES

I. THE REACTION OF ANTIMONY TRIFLUORIDE WITH PYROSULFURYL CHLORIDE

II. THE FLUORINATION OF METHOXYDICHLOROPHOSPHINE

BY

PHILIP JOSEPH PIZZOLATO

B.S., Loyola University, 1941
M.S., St. Louis University, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. THE REACTION OF ANTIMONY TRIFLUORIDE WITH PYROSULFURYL CHLORIDE

In the interest of furthering the knowledge of the chemical behavior of pyrosulfuryl chloride, a study of the fluorination of this compound was undertaken. Since the Swarts reaction (12) had been successfully applied to the fluorination of other sulfur oxyhalides, *e. g.*, thionyl and sulfuryl chlorides (5,3), its use in an attempt to fluorinate pyrosulfuryl chloride seemed the most logical starting point in this study.

The reaction was conducted in the usual Swarts generator (6), using sublimed antimony trifluoride as the fluorinating agent and antimony pentachloride as the catalyst. The "forcing" technique was employed to favor the formation of the partially fluorinated chlorofluoride. This technique consists in removing and collecting the gaseous products of the reaction from the generator flask as rapidly as they are formed (8,7,9). The first experiment was conducted with the reaction mixture at a temperature of about 50° C. and the pressure within the generator was maintained below 120 mm. (Hg). The fractional distillation of the reaction products revealed that considerable decomposition had taken place and that neither of the desired fluorine derivatives had been produced. The main product of the reaction was sulfuryl chlorofluoride, which was obtained in a yield of about 65 per cent and which was formed presumably by the fluorination of a decomposition product, sulfuryl chloride. Other products, isolated in small amounts, were sulfuryl chloride, sulfur dioxide, and chlorine.

When the above reaction at reduced pressure failed to produce the desired fluorine derivatives, a modification of this procedure in which the reaction is carried out under pressure was used. The technique and generator apparatus used were essentially the same as used earlier by Booth and Herrmann in the fluorination of sulfuryl chloride (3). Two experiments

were carried out under pressure: the first at about 40 p. s. i., the second at about 90. Results were similar to those obtained in the low pressure reaction; the fractional distillations of reaction products yielded again as the main product, sulfuryl chlorofluoride (about 47 per cent and 34 per cent yields in two experiments) and smaller amounts of the decomposition products encountered earlier.

Finally, in an attempt to determine whether the desired fluorine derivatives were stable under ordinary conditions an effect was made to obtain them by another, unrelated method: the chlorofluoride by the dehydration of an equimolar mixture of fluosulfonic and chlorosulfonic acids by means of phosphorus pentoxide; and the difluoride by the dehydration of fluosulfonic acid. Neither the chlorofluoride nor the difluoride could be obtained in this way.

Although definite evidence is lacking, the results of this investigation suggest, at least, that fluorine-containing pyrosulfuryl halides are considerably less stable than the known dichloride, possibly as a result of the weakening of an intermediary sulfur to oxygen bound by an adjacent sulfur to fluorine bond.

II. FLUORINATION OF METHOXYDICHLORO-PHOSPHINE

The applicability of the Swarts reaction to the fluorination of non-polar inorganic halides has been known for some time. Only in recent years, however, has there been any effort to evaluate the effect of organic substituents on the fluorination of derivatives of these compounds. The results of a study of the fluorination of alkyl chlorosilanes were reported in 1946 by Booth and coworkers (2). The effect of fluorination on the properties of alkyl substituted halides of sulfur, selenium, and tellurium has been studied by Emeléus and Heal (10). More recently, fluoride derivatives of phosphorus (V) ethoxysulfo-

dichloride were synthesized by Booth, Martin, and Kendall (4). For the purpose of extending the knowledge obtained in these earlier studies, a comparison of the results already observed in the fluorination of phosphorus (III) halides (1) with those for the fluorination of an alkoxy derivative of such a halide seemed desirable. With this objective in mind, a study of the fluorination of methoxydichlorophosphine was undertaken.

Although first prepared over fifty years ago (11), methoxydichlorophosphine has not been very well characterized. Therefore it seemed advisable to characterize this compound in much the same way as its fluoride derivatives.

Methoxydichlorophosphine was synthesized by adding dropwise one mole anhydrous methanol to one mole of phosphorus (III) chloride with vigorous stirring at a reaction temperature well below 0° C. After the addition of methanol was completed, the temperature of the reaction products was allowed to rise slowly to room temperature. Purified methoxydichlorophosphine was separated by fractional distillation in a yield of about 60 per cent.

The fluorination of methoxydichlorophosphine was conducted without a catalyst in a Swarts generator. The reaction temperature was maintained below 10° C. and for best yields of chlorofluoride and difluoride, the pressure within the generator was maintained below 50 mm. (Hg). Under these conditions methoxychlorofluorophosphine and methoxydifluorophosphine were obtained in yields of about 8 and 41 per cent respectively.

After fractional distillation the chemical analyses, freezing points, boiling points, vapor pressures, heats of vaporization, Trouton constants, and liquid densities were determined for methoxydichlorophosphine, and the chlorofluoro- and difluoroderivatives thereof.

Methoxydichlorophosphine and its chlorofluoride derivative are clear, colorless liquids; the difluoride is a colorless

gas which condenses to a clear, colorless liquid. Upon freezing, the dichloride and difluoride are transformed into white solids but the chlorofluoride forms a transparent glass.

SUMMARY OF THE PHYSICAL PROPERTIES

		CH_3OPCl_2	CH_3OPClF	CH_3OPF_2
Boiling Point, °C.		93.0	38.9	—15.5
Heat of Vaporization, g. cal./mole		8295	7077	5722
Trouton's Constant		22.7	22.7	22.2
Vapor Pressure Constants[a]	A	7.8300	7.8362	7.7335
	B	1812.6	1546.5	1250.5
Liquid density, d^0_4		1.406	1.318	——
Freezing Point, ± 0.4° C.		—91.0	glass[b]	—117.3

[a]Constants in the equation: $\log p_{mm.} = A - B/T$

[b]Glass forms at some temperature below — 79° C.

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VITA

The author was born in New Orleans, Louisiana, August 4, 1921. He attended St. Aloysius Elementary and High Schools there, graduating from the latter in June, 1937. He received the degree B. S. in chemistry from Loyola University of New Orleans June 2, 1941. He began graduate work at St. Louis University in September 1941 and held a graduate assistantship for the next two years. After receiving the degree Master of Science in chemistry from St. Louis University in May, 1943, he entered the University of Pittsburgh and held a graduate assistantship there for two semesters. In 1944 he entered the United States Navy and served in the American and Asiatic-Pacific Theaters. He was released to inactive duty in October, 1946 and entered the Graduate College of the University of Illinois in February, 1947. He held a third-year University Fellowship in the academic year 1948-1949.